

General Considerations on the Finite-Size Corrections for Coulomb Systems in the Debye–Hückel Regime

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Abstract

We study the statistical mechanics of classical Coulomb systems in a low coupling regime (Debye–Hückel regime) in a confined geometry with Dirichlet boundary conditions. We use a method recently developed by the authors which relates the grand partition function of a Coulomb system in a confined geometry with a certain regularization of the determinant of the Laplacian on that geometry with Dirichlet boundary conditions. We study several examples of confining geometry in two and three dimensions and semi-confined geometries where the system is confined only in one or two directions of the space. We also generalize the method to study systems confined in arbitrary geometries with smooth boundary. We find a relation between the expansion for small argument of the heat kernel of the Laplacian and the large-size expansion of the grand potential of the Coulomb system. This allow us to find the finite-size expansion of the grand potential of the system in general. We recover known results for the bulk grand potential (in two and three dimensions) and the surface tension (for two dimensional systems). We find the surface tension for three dimensional systems. For two dimensional systems our general calculation of the finite-size expansion gives a proof of the existence a universal logarithmic finite-size correction predicted some time ago, at least in the low coupling regime. For three dimensional systems we obtain a prediction for the perimeter correction to the grand potential of a confined system.

I Introduction

The study of confined classical Coulomb systems have attracted attention for some time in particular because in some cases they exhibit universal properties [1, 2, 3]. This universal behavior is present in some correlations functions [4] and also on the thermodynamic quantities of the Coulomb systems. In particular, the grand potential and thus the free energy, exhibit finite-size corrections

which depend on the confining domain [1]. Two particular cases have attracted attention: fully confined systems and semi-confined systems. On this respect we shall speak of semi-infinite or semi-confined systems to refer to systems which are confined only in a certain spatial direction (for example systems confined in a slab), to distinguish them from the totally confined systems. In both cases, exactly solvable models in two dimensions have allowed the explicit calculation of the finite-size corrections in the free energy for a given value of the coupling constant. For systems confined in a metallic slab of width W , in d dimensions, the free energy and the grand potential per unit area (times the inverse reduced temperature) exhibit an algebraic universal correction $C(d)/W^{d-1}$ with

$$C(d) = \frac{\Gamma(d/2)\zeta(d)}{2^d \pi^{d/2}} \quad (1.1)$$

where $\Gamma(z)$ and $\zeta(z)$ are the Gamma function and the Riemann zeta function respectively. This has been shown [1] to hold for any general Coulomb system provided that the system is in a conducting phase and it has good screening properties. It has also been checked in several solvable models. The correction is universal in the sense that it does not depend on the details of the microscopic constitution of the system.

For two-dimensional fully confined Coulomb systems there are also universal finite-size corrections which are similar to those of two dimensional critical systems. This lead us to another interesting feature of conducting classical Coulomb systems, which is its manifest similarity with critical systems [1, 3]. Although the particle and charge correlation functions of the Coulomb system are short-ranged because of the screening, it has been shown that the correlations of the electric field and the electric potential are long ranged [4, 5]. In this sense they can be considered as critical systems and they share properties of statistical models at criticality. For example, in two dimensions conformal field theory, which has proved to describe and classify correctly critical systems, predicts the existence of universal corrections in the free energy for critical systems due to their finite-size [6, 7, 8]. Explicitly, for any two-dimensional statistical system in its critical point confined in a domain of characteristic size R with smooth boundary, the free energy F has a large- R expansion of the form [6, 7]

$$\beta F = AR^2 + BR - \frac{c\chi}{6} \ln R + \dots \quad (1.2)$$

where $\beta = 1/(k_B T)$ with T the absolute temperature and k_B the Boltzmann constant. The first two terms AR^2 and BR represent respectively the bulk free energy and the “surface” (perimeter in two dimensions) contribution to the free energy. In general, the coefficients A and B are non-universal (they depend on the microscopic detail of the model under consideration) but the dimensionless coefficient of $\ln R$ is highly universal depending only on the Euler characteristic of the manifold $\chi = 2 - 2h - b$, where h is the number of handles and b is the number of boundaries, and on c the central charge of the model. For Coulomb systems the existence of a similar expansion, which reads

$$\beta F = AR^2 + BR + \frac{\chi}{6} \ln R + \dots \quad (1.3)$$

has been shown to hold in several exactly solvable models at a fixed value of the coulombic coupling constant [1, 3, 9, 10, 11] and in some particular geometries for any value of the coupling [12, 13, 14, 15].

In a previous paper [16] we considered two-dimensional Coulomb systems in a low coupling regime, the Debye–Hückel regime. We computed the grand potential for systems confined in two simple geometries, the disk and the annulus with ideal conductor boundaries, and confirmed the validity of the finite-size expansion (1.3) in those cases. We showed that the grand canonical partition function for a classical Coulomb system in the Debye–Hückel regime, confined with ideal grounded conductor boundaries, can be expressed as an infinite product of functions of the eigenvalues of the Laplace operator satisfying Dirichlet boundary conditions. The explicit form of this spectrum and the corresponding infinite products, depend on the shape of the confining domain, and must be calculated for each particular geometry. By a careful calculation of these infinite products we obtained the explicit form of the grand potential for Coulomb systems confined in a disk and in an annulus. When these systems are large we computed the finite-size expansion of the grand potential and we found the universal correction predicted by Eq. (1.3). The first purpose of the present paper is to apply this method to other particular cases of confining geometry including semi-confined systems and also to systems in three dimensions, for which conformal field theory predictions do not apply.

The second purpose this paper has to do with the fact that, from a more general point of view, it is possible to define a spectral function for the Laplacian, the heat kernel, that turns out to have an asymptotic behavior for small argument which is independent of the explicit form of the eigenvalues [17, 18]. Making use of these results, it is possible to show that the spectrum of the Laplace operator calculated on a given manifold endowed with a metric, contain geometrical information about the manifold itself. In this paper we use those ideas to obtain the large-size expansion of the grand potential for Coulomb systems confined in arbitrary geometries. Our results for the particular cases agree with the predictions of this general formalism.

This paper is organized as follows. In section II we summarize a few results of our previous paper [16] concerning the calculation of the grand potential for Coulomb systems in the Debye–Hückel regime in given confining geometries. In particular, we briefly describe how the grand potential can be obtained in terms of an infinite product of functions of the eigenvalues of the Laplace operator. In sections III and IV we apply the general method from Ref. [16] reviewed in section II. In section III we apply the method to some particular examples of confined and semi-confined systems in two and three dimensions. In section IV we consider the general case of fully confined systems in an arbitrary geometry. We relate the grand potential of the system to the zeta regularization of the determinant of the Laplacian. By using the known results [17, 18] for the asymptotic expansion of the heat kernel we find in general the finite-size expansion of the grand potential and, for two-dimensional systems, we confirm the existence of the predicted universal finite-size expansion. At the end of that section we present an illustration of this latter method by considering the case

of a Coulomb system confined in a large square, and we recover a finite-size correction predicted by conformal field theory. Sections III and IV are mostly independent and the reader not interested in the examples of section III can proceed directly to the general treatment exposed in section IV. In section V we present a summary and gather some conclusions.

II Summary of Previous Results

Let us start by describing the model under consideration. Our system is a multi-component Coulomb gas living in d dimensions and composed of s species of charged particles $\alpha = 1, \dots, s$ each of which have N_α particles of charge q_α . The system is confined in a domain of volume V with ideal conductor boundaries. We shall describe these systems using classical (i.e. non-quantum) statistical mechanics in the grand canonical ensemble. The average densities of the particles n_α are therefore controlled by the fugacities ζ_α . We shall impose the pseudo-neutrality condition

$$\sum_{\alpha} q_{\alpha} \zeta_{\alpha} = 0 \quad (2.1)$$

which implies that at the mean field level the system is neutral and there is no potential difference between the system and the boundaries. In the appendix B of Ref. [16] we explain what happens in the more general case when the condition (2.1) is not satisfied.

The interaction potential between two unit charges located at \mathbf{r} and \mathbf{r}' is given by the Coulomb potential $v(\mathbf{r}, \mathbf{r}')$ which is the solution of Poisson equation

$$\Delta v(\mathbf{r}, \mathbf{r}') = -s_d \delta(\mathbf{r} - \mathbf{r}') \quad (2.2)$$

satisfying Dirichlet boundary conditions and where $s_d = 2\pi^{d/2}/\Gamma(d/2)$, that is in two dimensions $s_2 = 2\pi$ and for three dimensional systems $s_3 = 4\pi$. For non-confined systems the Coulomb potential reads

$$v^0(\mathbf{r}, \mathbf{r}') = \begin{cases} \frac{1}{|\mathbf{r} - \mathbf{r}'|}, & \text{if } d = 3 \\ -\ln \frac{|\mathbf{r} - \mathbf{r}'|}{L}, & \text{if } d = 2 \end{cases} \quad (2.3)$$

where L is an arbitrary length scale which fixes the zero of the Coulomb potential in two dimensions. For the confined system under consideration the explicit form of the Coulomb potential should be modified in order to satisfy the Dirichlet boundary conditions.

As explained in Ref. [16] (see also [19]), the potential energy of the system can be written as

$$\begin{aligned} H &= \frac{1}{2} \sum_{\alpha, \gamma} \sum'_{i, j} q_{\alpha} q_{\gamma} v(\mathbf{r}_{\alpha, i}, \mathbf{r}_{\gamma, j}) + \frac{1}{2} \sum_{\alpha} \sum_i q_{\alpha}^2 [v(\mathbf{r}_{\alpha, i}, \mathbf{r}_{\alpha, i}) - v^0(\mathbf{r}_{\alpha, i}, \mathbf{r}_{\alpha, i})] \\ &= \frac{1}{2} \sum_{\alpha, \gamma} \sum_{i, j} q_{\alpha} q_{\gamma} v(\mathbf{r}_{\alpha, i}, \mathbf{r}_{\gamma, j}) - \frac{1}{2} \sum_{\alpha} \sum_i q_{\alpha}^2 v^0(\mathbf{r}_{\alpha, i}, \mathbf{r}_{\alpha, i}) \end{aligned} \quad (2.4)$$

In the first line the prime in the first summation means that the case when $\alpha = \gamma$ and $i = j$ must be omitted. The first term is the usual inter-particle energy between pairs. The second term is the Coulomb energy of a particle and the polarization surface charge density that the particle has induced in the boundaries of the system.

In Ref. [16] we performed the sine-Gordon transformation [20] on the grand canonical partition function Ξ of the system. Then we expanded the action around the mean field solution to the quadratic order in the field. This is valid in the Debye-Hückel regime. Then the remaining functional integral can be performed easily since it is a Gaussian. The result is a certain determinant involving the Laplacian which we put in the form

$$\Xi = \left(\prod_m \left(1 - \frac{\kappa^2}{\lambda_m} \right) \prod_n e^{\frac{\kappa^2}{\lambda_n^0}} \right)^{-1/2} e^{\sum_\alpha V \zeta_\alpha}. \quad (2.5)$$

where $\kappa^{-1} = (\sum_\alpha s_d \zeta_\alpha \beta q_\alpha^2)^{-1/2}$ equals the Debye length in this regime, λ_m denotes the Laplacian eigenvalues satisfying the Dirichlet boundary conditions and $\lambda_n^0 = -\mathbf{K}^2$, $\mathbf{K} \in \mathbb{R}^d$, refers to the (continuum) eigenvalues of the Laplacian in the non-confined case. These come from the “subtraction” of the self-energy term $v^0(\mathbf{r}, \mathbf{r})$ in Eq. (2.4).

Each infinite product in (2.5) diverges separately. Indeed they are ultraviolet divergent for large values of $|\lambda_m|$ and $|\lambda_n^0|$. However, when they are putted together as in (2.5), the divergences cancel each other (at least for the bulk properties of the system). In three dimensions we can find immediately a well defined expression for the grand potential from $\Omega = -k_B T \ln \Xi$. In two dimensions, the situation is a bit more involved since certain infrared divergence appear in the second product and it must be regularized by introducing a lower cutoff. In Ref. [16] we explained how to deal with this case and we found the value of this cutoff explicitly in terms of the constant L which fixes the zero of the Coulomb potential, which needs to be supposed to be large. This cutoff was found to be given by $k_{\min} = 2e^{-C}/L$ where C is the Euler constant. From Ref. [16], we recall that for a non-confined system Eq. (2.5) gives for the bulk grand potential

$$\frac{\beta \Omega_b}{V} = \frac{\kappa^2}{4\pi} \left[-\ln \frac{\kappa L}{2} - C + \frac{1}{2} \right] - \sum_\alpha \zeta_\alpha \quad (2D) \quad (2.6)$$

$$\frac{\beta \Omega_b}{V} = -\frac{\kappa^3}{12\pi} - \sum_\alpha \zeta_\alpha \quad (3D) \quad (2.7)$$

in two and three dimensions respectively. These expressions agree with results by the usual formulation of the Debye-Hückel theory [21, 22, 23].

III Solved Examples

III.1 Systems in Two Dimensions

In Ref. [16] using Eq. (2.5) we computed the grand potential of a two-dimensional Coulomb system confined in a disk and in an annulus, and we confirmed that its finite-size expansion is of the form

$$\beta\Omega = \beta\Omega_b + \beta\gamma + \frac{\chi}{6} \ln(\kappa R) + O(1) \quad (3.1)$$

with Ω_b given by Eq. (2.6). The surface (perimeter) tension is

$$\gamma = -k_B T \kappa / 8. \quad (3.2)$$

We notice the existence of the universal finite-size correction $(\chi/6) \ln R$ with the Euler characteristic $\chi = 1$ for the disk and $\chi = 0$ for the annulus.

In this section we will consider an additional example of confining geometry in two dimensions.

III.1.1 Space Between Two Infinite Lines: The Slab in Two Dimensions

The method outlined in section II can be used to study semi-confined systems. In this subsection we consider the case of such a system in two dimensions. The geometry consists of two infinite parallel lines spaced by a distance W and the Coulomb systems is confined in between these two lines. We assume Dirichlet boundary conditions for the electric potential. Let us assume that the lines are in the direction of the y -axis and the x -axis is perpendicular to the lines. If we write the Laplacian eigenvalues as $\lambda = -k_x^2 - k_y^2$, these take discrete values only in the k_x direction. The eigenfunctions can be written as $\Psi(x, y) \propto e^{i(k_y y)} \sin(k_x x)$, satisfying the boundary conditions $\Psi(0, y) = 0$ and $\Psi(W, y) = 0$, which imply $k_x = n\pi/W$ with n a positive, non-zero, integer. In the direction of the y -axis there is no confinement therefore $k_y \in \mathbb{R}$. Then, the eigenvalues of the Laplace operator are given by $\lambda_{n, k_y} = -(n\pi/W)^2 - k_y^2$, for $n = 1, 2, \dots$, and $k_y \in \mathbb{R}$. Introducing the explicit form of the eigenvalues in (2.5) we have the grand potential expressed as

$$\beta\Omega = \frac{1}{2} \frac{l}{(2\pi)} \int_{-\infty}^{\infty} \ln \prod_{n=1}^{\infty} \left(1 + \frac{\kappa^2}{\left(\frac{n\pi}{W}\right)^2 + k_y^2} \right) dk_y + \frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_{\alpha} V \zeta_{\alpha} \quad (3.3)$$

where l is the dimension of the system in the y -direction. The second term in (3.3) involve the spectrum for a non-confined system, $\lambda^{(0)} = -\mathbf{K}^2$ with $\mathbf{K} \in \mathbb{R}^2$. It can be written as $\frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} = -\frac{V\kappa^2}{4\pi} \int_{k_{\min}}^{K_{\max}} \frac{dK}{K}$, where $V = lW$ is the “volume” (area) of the system between a portion of length l of the confining lines. The lower limit for this integral is $k_{\min} = 2e^{-C}/L$ as mentioned in section II and explained in Ref. [16]. Also as explained earlier this integral is ultraviolet

divergent therefore we introduced an ultraviolet cutoff K_{\max} . In the first term of Eq. (3.3) the infinite product converges to a known expression [24] giving

$$\beta\Omega = \frac{l}{2\pi} \int_0^{k_{\max}} \ln \frac{k_y \sinh \left(W \sqrt{\kappa^2 + k_y^2} \right)}{\sqrt{\kappa^2 + k_y^2} \sinh(k_y W)} dk_y - \frac{Wl\kappa^2}{4\pi} \int_{k_{\min}}^{K_{\max}} \frac{dK}{K} - \sum_{\alpha} V\zeta_{\alpha} \quad (3.4)$$

where we also introduced an ultraviolet cutoff for the first integral k_{\max} . Both cutoffs k_{\max} and K_{\max} should be proportional and their exact relation can be found by requiring that in the limit $W \rightarrow \infty$ we recover the known bulk value of the grand potential (2.6). Performing some of the integrals in (3.4) we find that the grand potential per unit length $\omega = \Omega/l$ is given by

$$\begin{aligned} \beta\omega &= \frac{\kappa^2 W}{4\pi} \ln \frac{2k_{\max}}{K_{\max}} + \frac{\kappa^2 W}{4\pi} \left[\frac{1}{2} - \ln \frac{\kappa L}{2e^{-C}} \right] - W \sum_{\alpha} \zeta_{\alpha} \\ &\quad - \frac{\kappa}{4} + \frac{\pi}{24W} + \int_0^{\infty} \ln \left(1 - e^{-2W\sqrt{\kappa^2 + k_y^2}} \right) \frac{dk_y}{2\pi} \end{aligned} \quad (3.5)$$

where all terms that vanish when $k_{\max} \rightarrow \infty$ have been omitted. Therefore to recover the known value (2.6) of the bulk grand potential in the limit $W \rightarrow \infty$ the ultraviolet cutoffs should be related by $K_{\max} = 2k_{\max}$. Using these cutoffs we finally find the grand potential and its finite-size expansion

$$\beta\omega = \beta\omega_b + 2\beta\gamma + \frac{\pi}{24W} + \int_0^{\infty} \ln \left(1 - e^{-2W\sqrt{\kappa^2 + k_y^2}} \right) \frac{dk_y}{2\pi} \quad (3.6a)$$

$$= \beta\omega_b + 2\beta\gamma + \frac{\pi}{24W} + O(e^{-2\kappa W}) \quad (3.6b)$$

where $\omega_b = \Omega_b/l$ with the bulk grand potential Ω_b given by Eq. (2.6). The surface tension γ is given by Eq. (3.2), which is the same surface tension that we found in the case of the disk and the annulus in our previous work [16] as expected. Finally, we also found the universal finite-size correction for the case of the slab in two dimensions, which turns out to be $\pi/(24W) = \zeta(2)/(4\pi W)$ in accordance with the general prediction from Ref. [1]: $\Gamma(d/2)\zeta(d)/(2^d \pi^{d/2} W^{d-1})$ for $d = 2$ as expected.

III.2 Systems in Three Dimensions

In this section we consider some examples of three-dimensional Coulomb systems first confined in a slab geometry then inside a ball and inside a spherical thick shell.

III.2.1 Space Between Two Infinite Planes: The Slab in Three Dimensions

We begin the study of particular examples of three-dimensional systems by considering a system confined in the space between two infinite parallel planes,

separated by a distance W . Taking the x -coordinate along the direction normal to the planes we find that the eigenfunctions are $\Psi(\mathbf{r}) \propto e^{i(\mathbf{k}_\perp \cdot \mathbf{r}_\perp)} \sin(k_x x)$, where $\mathbf{k}_\perp \cdot \mathbf{r}_\perp = yk_y + zk_z$, and satisfying the boundary conditions $\Psi(0, y, z) = 0 = \Psi(W, y, z)$. Thus, the eigenvalues are given by $k_x = n\pi/W$, with $n = 1, 2, \dots$, and $k_y \in \mathbb{R}$ and $k_z \in \mathbb{R}$. Using (2.5) and the explicit form of the eigenvalues we have

$$\beta\Omega = \frac{1}{2} \frac{A}{(2\pi)^2} \int \ln \prod_{n=1}^{\infty} \left(1 + \frac{\kappa^2}{\left(\frac{n\pi}{W}\right)^2 + \mathbf{k}_\perp^2} \right) d\mathbf{k}_\perp + \frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_\alpha V\zeta_\alpha \quad (3.7)$$

where A represents the area of the planes. The second term coming from the subtraction of the self-energy is now

$$\frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} = -\frac{1}{2} \frac{\kappa^2 V}{(2\pi)^3} \int d\tilde{\Omega} \int_0^{K_{\max}} \frac{k^2 dk}{k^2} = -\frac{\kappa^2 V}{(2\pi)^2} K_{\max} \quad (3.8)$$

where $V = AW$ is the volume of the system. As in the two-dimensional example we introduced an ultraviolet cutoff K_{\max} .

Similarly to the two-dimensional slab, the infinite product in the first term converges to [24]

$$\prod_{n=1}^{\infty} \left(1 + \frac{\kappa^2}{\left(\frac{n\pi}{W}\right)^2 + \mathbf{k}_\perp^2} \right) = \frac{k_\perp}{\sqrt{\kappa^2 + \mathbf{k}_\perp^2}} \frac{\sinh\left(W\sqrt{\kappa^2 + \mathbf{k}_\perp^2}\right)}{\sinh(k_\perp W)} \quad (3.9)$$

with $k_\perp = |\mathbf{k}_\perp|$. The remaining integral over \mathbf{k}_\perp is ultraviolet divergent and must be cutoff to a maximum value k_{\max} for k_\perp . In the limit $k_{\max} \rightarrow \infty$ we have

$$\frac{\beta\Omega}{A} = \left[\frac{\kappa^2}{8\pi} \left(k_{\max} - \frac{2K_{\max}}{\pi} \right) - \frac{\kappa^3}{12\pi} - \sum_\alpha \zeta_\alpha \right] W \quad (3.10)$$

$$+ \frac{\kappa^2}{8\pi} \left[\ln \frac{\kappa}{k_{\max}} - \frac{1}{2} \right] \quad (3.11)$$

$$+ \frac{\zeta(3)}{16\pi W^2} + \frac{1}{4\pi} \int_0^\infty k \ln(1 - e^{-2W\sqrt{k^2 + \kappa^2}}) dk \quad (3.12)$$

From this expression we see that the ultraviolet cutoffs should be related by $k_{\max} = 2K_{\max}/\pi$ in order to recover the known value of the bulk grand potential (2.7) in the limit $W \rightarrow \infty$. Then the grand potential is finally given by

$$\frac{\beta\Omega}{A} = \frac{\beta\Omega_b}{A} + 2\beta\gamma + \frac{\zeta(3)}{16\pi W^2} + \frac{\kappa^2}{4\pi} \int_1^\infty u \ln(1 - e^{-2u\kappa W}) du \quad (3.13a)$$

$$\stackrel{W \rightarrow \infty}{=} \frac{\beta\Omega_b}{A} + 2\beta\gamma + \frac{\zeta(3)}{16\pi W^2} + O(e^{-2\kappa W}) \quad (3.13b)$$

with the bulk grand potential Ω_b given by Eq. (2.7) and the surface tension γ given by

$$\beta\gamma = \frac{\kappa^2}{16\pi} \left[\ln \frac{\kappa}{k_{\max}} - \frac{1}{2} \right] \xrightarrow{k_{\max} \rightarrow \infty} \frac{\kappa^2}{16\pi} \ln \frac{\kappa}{k_{\max}} \quad (3.14)$$

Note that when we take the limit $k_{\max} \rightarrow \infty$ the surface tension diverges with the cutoff as $-\kappa^2/(16\pi) \ln k_{\max}$. This divergence in the surface tension can be understood if we note that the particles tend to move to the frontiers because of the ideal conductor character of the boundaries. This is easy to see from a physical argument: the ideal conductor boundaries condition is equivalent to introduce an image charge of opposite sign at the other side of the boundary for each particle in the system. Particles near the boundary “feel” an attraction to the boundary due to their proximity with their corresponding images. Near a boundary, the density of the species α at a distance X from the boundary will behave in this low coupling approximation as the linearized Boltzmann factor of the particle-image interaction $1 + \beta q_\alpha^2/(4X)$. At large distances this interaction is screened but at short distances it remains non-integrable. Since the surface tension can be obtained as an integral of the density profile [25], this surface tension will be infinite. Imposing a short-distance cutoff D for the minimum approach of the particles to the wall, will give a the surface tension which diverges as $\ln D$. Our ultraviolet cutoff k_{\max} is proportional to $1/D$. For details see Ref. [19]. Notice that, on the other hand, for a two-dimensional system the surface tension does not diverge with the cutoff (see Ref. [16] and section III.1.1). In two dimensions the particle-image interaction is $[q_\alpha^2/2] \ln(2X/L)$ and this expression is integrable at short-distances. This explains why the surface tension is finite and cutoff independent for two-dimensional systems although the particles are strongly attracted to the boundaries contrary to the situation in three dimensions where the surface tension diverges with the cutoff.

Returning to Eq. (3.13b) we found a finite-size correction depending on W^{-2} . This agree with the universal finite-size correction for a slab in d -dimensions, Eq. (1.1), for $d = 3$ predicted in Ref. [1].

III.2.2 Coulomb System Inside a Ball

We continue the study of finite-size Coulomb systems calculating the grand potential for a three-dimensional Coulomb system confined inside a spherical domain. The eigenvalue problem for the Laplace operator in this case is easily solved. The eigenfunctions are $\Psi(r, \theta, \varphi) = \sqrt{\pi/(2r\lambda^{1/2})} I_{l+1/2}(\sqrt{\lambda}r) Y_{lm}(\theta, \varphi)$ where $I_{l+1/2}$ are the modified Bessel functions of half integer order and Y_{lm} are the spherical harmonics. The eigenvalues λ are determined from the Dirichlet boundary condition $\Psi(R, \theta, \varphi) = 0$ where R is the radius of the sphere. Thus, the eigenvalues are the roots of the equation $I_{l+1/2}(\sqrt{\lambda}R) = 0$. Let us call $\nu_{l+1/2,n}$ the zeros of $I_{l+1/2}$. Then the eigenvalues are given by $\lambda_k = \nu_{l+1/2,n}^2/R^2$ for $l = 0, 1, 2, \dots$ and $n = 1, 2, \dots$. Also for each value of l and n , the corresponding eigenvalue is degenerated $2l + 1$ times. Then, the expression for the grand

potential obtained from (2.5) takes the form

$$\beta\Omega = \frac{1}{2} \ln \left[\prod_{l=0}^{\infty} \left(\prod_{n=1}^{\infty} \left(1 - \frac{z^2}{\nu_{l+1/2,n}^2} \right) \right)^{2l+1} \right] + \frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_{\alpha} V \zeta_{\alpha} \quad (3.15)$$

where the indexes n and $l + 1/2$ denote the root and the order of the modified Bessel function $I_{l+1/2}$ respectively and $z = \kappa R$. The infinite product over the index n can be performed exactly [24]

$$\prod_{n=1}^{\infty} \left(1 - \frac{z^2}{\nu_{l+1/2,n}^2} \right) = \Gamma \left(l + \frac{3}{2} \right) \left(\frac{2}{z} \right)^{l+1/2} I_{l+1/2}(z). \quad (3.16)$$

The remaining summation over the index l diverges and we must regularize it by introducing an upper cutoff N on l .

The second term coming from the subtraction of the self energy is

$$\frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} = -\frac{1}{2} \frac{\kappa^2 V}{(2\pi)^3} \int d\Omega \int_0^{K_{\max}} \frac{k^2 dk}{k^2} = -\frac{\kappa^2}{3\pi} R^3 K_{\max} \quad (3.17)$$

where $V = \frac{4}{3}\pi R^3$ is the volume of the system. As in the previous examples we introduced an ultraviolet cutoff K_{\max} which must be proportional to N in order to cancel the divergences. The exact relation between K_{\max} and N is found by the requirement that the bulk value of the grand potential (2.7) is recovered in the limit $R \rightarrow \infty$.

To find the finite-size expansion of the grand potential we make use of the Debye uniform asymptotic expansion [26] for the Bessel functions, valid for large values of the argument,

$$\ln I_{\nu}(z) = -\frac{1}{2} \ln(2\pi) - \frac{1}{4} \ln(z^2 + \nu^2) + \eta(\nu, z) + \frac{3u - 5u^3}{24\nu} + o\left(\frac{1}{z^2 + \nu^2}\right) \quad (3.18)$$

with

$$\eta(\nu, z) = (z^2 + \nu^2)^{1/2} - \nu \sinh^{-1} \left(\frac{\nu}{z} \right); \quad u = \frac{\nu}{(z^2 + \nu^2)^{1/2}} \quad (3.19)$$

together with the Euler-McLaurin summation formula to transform the summation into an integral: $\sum_{l=0}^N f(l) = \int_0^N f(l) dl + \frac{1}{2} [f(0) + f(N)] + \frac{1}{12} [f'(N) - f'(0)] + \dots$, and the Stirling asymptotic expansion for the Gamma function. Then in the limit $N \rightarrow \infty$ and $z \rightarrow \infty$ we find

$$\beta\Omega = \beta\Omega_{\text{bulk}} + \left(1 + 2 \ln \frac{R\kappa}{N} \right) \frac{\kappa^2 R^2}{8} + \frac{\kappa R}{3} + O(R^0) + o(N^0) \quad (3.20)$$

where

$$\beta\Omega_{\text{bulk}} = \left[-\frac{\kappa^3}{12\pi} + \frac{3\kappa^2}{16\pi} \frac{N}{R} - \frac{\kappa^2}{4\pi^2} K_{\max} - \sum_{\alpha} \zeta_{\alpha} \right] V \quad (3.21)$$

This value of the bulk grand potential should be equal to the one given by Eq. (2.7) therefore $K_{\max} = (3\pi/4)N/R$. The ultraviolet cutoff K_{\max} is indeed proportional to the cutoff N and with this relation between the cutoffs the bulk divergences of the first and second terms in the r.h.s. of (3.15) cancel each other. Reporting the result for K_{\max} in (3.21) we find

$$\beta\Omega = \left[-\frac{\kappa^3}{12\pi} - \sum_{\alpha} \zeta_{\alpha} \right] \frac{4\pi}{3} R^3 + \left(\frac{\kappa^2}{32\pi} + \frac{\kappa^2}{16\pi} \ln \frac{\kappa R}{N} \right) 4\pi R^2 + \frac{\kappa}{3} R + o(R). \quad (3.22)$$

The first term in the r.h.s. of Eq. (3.22) is the bulk grand potential in three dimensions. In the second term, the expression in parenthesis gives the surface tension for the system and the third term is a (non-universal) perimeter contribution. Notice again that the surface tension diverges as $-\kappa^2/(16\pi) \ln K_{\max}$ with the cutoff.

III.2.3 Spherical Shell

We consider now the case of a three-dimensional Coulomb system confined inside a spherical shell. Let a and b be the inner and outer radii of the shell respectively. As in the previous example, the eigenfunctions $\Psi(r, \theta, \varphi)$ are separable in a radial and an angular part. The eigenfunctions of the Laplacian for this geometry are $\Psi(r, \theta, \varphi) = \left[A \sqrt{\frac{\pi}{2r\lambda^{1/2}}} I_{l+1/2}(\sqrt{\lambda}r) + B \sqrt{\frac{\pi}{2r\lambda^{1/2}}} K_{l+1/2}(\sqrt{\lambda}r) \right] Y_{lm}(\theta, \varphi)$. The eigenvalues are determined by the boundary conditions $\Psi(a, \theta, \varphi) = \Psi(b, \theta, \varphi) = 0$, that is $AI_{l+1/2}(\sqrt{\lambda}a) + BK_{l+1/2}(\sqrt{\lambda}a) = 0 = AI_{l+1/2}(\sqrt{\lambda}b) + BK_{l+1/2}(\sqrt{\lambda}b)$. These two equations can be considered as a linear system of equations for the coefficients A and B . It has a non-trivial solution if and only if

$$I_{l+1/2}(\sqrt{\lambda}a)K_{l+1/2}(\sqrt{\lambda}b) - I_{l+1/2}(\sqrt{\lambda}b)K_{l+1/2}(\sqrt{\lambda}a) = 0. \quad (3.23)$$

The roots of this equation gives the eigenvalues. Let $\vartheta_{l,n}$ be the n -th root of $I_{l+1/2}(za)K_{l+1/2}(zb) - I_{l+1/2}(zb)K_{l+1/2}(za) = 0$ for $l = 0, 1, 2, \dots$. Then we have $\lambda_k = \vartheta_{l,n}^2$. Each eigenvalue is $(2l+1)$ -degenerated. Then the expression for the grand potential takes the form

$$\beta\Omega = \frac{1}{2} \ln \left[\prod_{l=0}^{\infty} \prod_{n=1}^{\infty} \left(1 - \frac{\kappa^2}{\vartheta_{l,n}^2} \right)^{2l+1} \right] + \frac{1}{2} \sum_k \frac{\kappa^2}{\lambda_k^0} - \sum_{\alpha} V \zeta_{\alpha} \quad (3.24)$$

The infinite product over the index n can be performed explicitly by using a method explained in Refs. [27, 10, 16]. Let us consider the entire function

$$f_l(z) = (2l+1) \frac{I_{l+1/2}(za)K_{l+1/2}(zb) - I_{l+1/2}(zb)K_{l+1/2}(za)}{\left[\left(\frac{a}{b} \right)^{l+1/2} - \left(\frac{b}{a} \right)^{l+1/2} \right]} \quad (3.25)$$

which has the following properties: $f_l(z) = f_l(-z)$, $f_l(0) = 1$, $f'_l(0) = 0$ and its zeros are $\vartheta_{l,n}$. Therefore it admits an expansion as a Weierstrass infinite

product

$$f_l(z) = \prod_{n=1}^{\infty} \left(1 - \frac{z^2}{\vartheta_{l,n}^2} \right). \quad (3.26)$$

Then the product we need to compute is simply $f_l(\kappa)$. The grand potential then takes the form

$$\beta\Omega = \frac{1}{2} \sum_{l=0}^N (2l+1) \ln f_l(\kappa) - \frac{\kappa^2}{3\pi} (b^3 - a^3) K_{\max} - \sum_{\alpha} V \zeta_{\alpha} \quad (3.27)$$

where we introduced the now familiar cutoffs N for the sum and K_{\max} for the integral. As in all the previous examples these cutoffs are proportional and their exact relation is found by requiring that in the limit of a large system we recover the known bulk value (2.7) of the grand potential.

For the calculation of the finite-size expansion of the grand potential, notice first that the contribution of $K_l(\kappa b)I_l(\kappa a)$ is of order $e^{-(b-a)\kappa}$, that is to say exponentially smaller than the contribution of the term $I_l(\kappa b)K_l(\kappa a)$ and as a consequence we can ignore it. To find the value of the remaining summation over the index l , we use the approximations of $K_{l+1/2}(\kappa a)$ and $I_{l+1/2}(\kappa b)$ for large values of the argument, which can be obtained from the Debye approximation for the modified Bessel functions [26]. Then we apply the Euler-McLaurin summation formula and take the limits $N \rightarrow \infty$, $b \rightarrow \infty$, $a \rightarrow \infty$ and $b-a \rightarrow \infty$ with $a/b < 1$ fixed. We find that the volume bulk part of the grand potential is given by

$$\beta\Omega_{\text{bulk}} = \frac{N\kappa^3}{4b\kappa} b^3 - \frac{N\kappa^3}{4a\kappa} a^3 - \left(\frac{\kappa}{9} + \frac{\kappa^2 k_{\max}}{3\pi} + \frac{4\pi}{3} \sum_{\alpha} \zeta_{\alpha} \right) (b^3 - a^3) \quad (3.28)$$

Equating this to the grand potential of the bulk system (2.7) we find

$$K_{\max} = \frac{3\pi}{4} \frac{N}{b} \frac{1 - (a^2/b^2)}{1 - (a^3/b^3)} \quad (3.29)$$

Using this relation we finally obtain

$$\beta\Omega = \beta\Omega_b + \beta\Omega_{\text{surface}} + \frac{1}{3} (b-a) \kappa + O(a^0) + O(b^0) \quad (3.30)$$

where Ω_b is given by Eq. (2.7) and

$$\beta\Omega_{\text{surface}} = \frac{1}{8} \left(2 \ln \frac{a\kappa}{N} - 3 \right) a^2 \kappa^2 + \frac{1}{8} \left(2 \ln \frac{b\kappa}{N} + 1 \right) b^2 \kappa^2 \quad (3.31)$$

Some additional comments are in order. The divergence in the surface tension, familiar to us at this point, is also present in this case. In the limit $K_{\max} \rightarrow \infty$ we have $\beta\Omega_{\text{surface}} \rightarrow -4\pi (b^2 + a^2) [\kappa^2/16\pi] \ln(K_{\max}/\kappa)$ which allows us to define a surface tension γ similar to the one of the previous other three-dimensional cases

$$\beta\gamma = -\frac{\kappa^2}{16\pi} \ln \frac{K_{\max}}{\kappa} \quad (3.32)$$

We find again a perimeter contribution to the grand which is not universal (it depends on the Debye length κ^{-1}). This time it is given by $k_B T \kappa (b - a)/3$. This clearly suggests that this perimeter correction is related to the curvature of the boundary and probably to the curvature of the space itself. This is indeed the case as we will show for any general geometry in the following section.

IV Grand Potential for Arbitrary Confining Geometries

Up to now we have been capable to find the explicit form of the grand potential for systems in specified confining geometries. Our calculations of last section always involve the resolution of the Laplacian eigenvalue problem for each specific geometry. From a more general point of view it is possible to define functions of the spectrum of the Laplacian that admit asymptotic expansions, that turn out to have some properties that are independent of the explicit form of the eigenvalues. Also in some cases these functions are related to some invariants of the confining manifold, for example in two dimensions to the Euler characteristic of the manifold. In this section we make use of those ideas to find the finite-size expansion of the grand potential in the case when the spectrum of the Laplacian in the confining geometry is not known explicitly.

IV.1 Spectral Functions of the Laplacian

In this section we review some spectral functions that will be useful for our analysis. Let \mathcal{M}_g be a Riemannian manifold endowed with a certain metric g and with boundary $\partial\mathcal{M}_g$ and Δ the Laplace operator defined on \mathcal{M}_g . The spectrum of \mathcal{M}_g is the set $\{0 \geq \lambda_0 \geq \lambda_1 \geq \dots \downarrow -\infty\}$ of eigenvalues of Δ , that satisfy $\Delta\Psi = \lambda\Psi$, where Ψ are the eigenfunctions of Δ . In order to determine the spectrum, these functions must satisfy certain boundary conditions on $\partial\mathcal{M}_g$ which we impose to be of the Dirichlet type, that is $\Psi = 0$ on $\partial\mathcal{M}_g$. The first spectral function we are interested in is the heat kernel defined as

$$\Theta(t) = \sum_{k=0}^{\infty} e^{t\lambda_k}, \quad (4.1)$$

which is convergent for $\Re(t) > 0$. It is known that the heat kernel admits an asymptotic expansion for $t \rightarrow 0$ of the form

$$\Theta(t) \sim \sum_{n=0}^{\infty} c_{i_n} t^{i_n}. \quad (4.2)$$

Here $\{i_n\}$ is a certain increasing sequence of real numbers and $i_0 < 0$. The exponent i_0 is particularly important because $c_{i_0} t^{i_0}$ is the divergent leading term in the series. According to the famous Weyl estimate [28] for the Laplacian $i_0 = -d/2$ where d is the dimension of the manifold and $(4\pi)^{d/2} c_{i_0}$ is the volume

of the manifold. Following Ref. [29] we define the order of the sequence of the eigenvalues as $\mu = -i_0 = d/2$. For a manifold \mathcal{M}_g with a smooth boundary, some of the terms in the small- t expansion of the heat kernel have been found by Kac and others [17, 18]

$$(4\pi t)^{d/2} \Theta(t) = V - \frac{\sqrt{4\pi t}}{4} B + \frac{t}{6} (2C + D) + o(t^{3/2}) \quad (4.3)$$

where

$$V = \text{the volume of } \mathcal{M}_g \quad (4.4)$$

$$B = \text{the surface area of } \partial\mathcal{M}_g \quad (4.5)$$

$$C = \text{the curvatura integra} = \int_{\mathcal{M}_g} K \quad (4.6)$$

$$D = \text{the integrated mean curvature} = \int_{\partial\mathcal{M}_g} J \quad (4.7)$$

where K is the scalar curvature at a point inside the domain \mathcal{M}_g and J is the mean curvature at a point in the boundary $\partial\mathcal{M}_g$. If we choose a metric g in which locally the first coordinate is perpendicular to the boundary and outward pointing to it then the mean curvature J can be computed as [18]¹

$$J = \partial_1 [g^{11} \det g] \sqrt{g_{11}} / \det g \quad (4.8)$$

Notice that in two dimensions the well-known Gauss–Bonnet theorem [30] states that $2C + D = 4\pi\chi$ where χ is the Euler characteristic of the manifold. Therefore in two dimensions the heat kernel expansion reads

$$\Theta(t) = \frac{V}{4\pi t} - \frac{B}{8\sqrt{\pi t}} + \frac{\chi}{6} + o(t^{1/2}) \quad (4.9)$$

The second spectral function we are interested in is the Fredholm determinant defined as $\prod_{k=0}^{\infty} \left(1 - \frac{a}{\lambda_k}\right)$ which is precisely the infinite product involved in the calculation of the grand potential of the Coulomb system from Eq. (2.5). Unfortunately this infinite product only converges for sequences of order $\mu < 1$, and therefore it diverges for the cases we are interested in, when $\mu = 1$ (two dimensions) and $\mu = 3/2$ (three dimensions). For the cases $\mu > 1$ a Weierstrass canonical regularization of the Fredholm determinant reads [29]

$$F(a) = \prod_{k=0}^{\infty} \left(1 - \frac{a}{\lambda_k}\right) \exp \left[\frac{a}{\lambda_k} + \frac{a^2}{2\lambda_k^2} + \dots + \frac{a^{[\mu]}}{[\mu]\lambda_k^{[\mu]}} \right] \quad (4.10)$$

which is valid for $\mu > 1$, where $[\mu]$ is the integer part of μ . The exponential term in (4.10) is introduced in order to make the infinite product convergent

¹Notice that we use here the convention of outward pointing normal vectors to the boundary. This is the opposite convention as the one in Ref. [18]: our J is minus the J of Ref. [18].

when the order of the sequence is larger than one. We are interested in two- and three-dimensional manifolds when μ equals 1 or $3/2$ respectively. In both cases expression (4.10) reduces to

$$F(a) = \prod_{k=0}^{\infty} \left(1 - \frac{a}{\lambda_k}\right) e^{a/\lambda_k}. \quad (4.11)$$

Although, strictly speaking the product (4.10) is only defined for $\mu > 1$ we will still use it in the two dimensional case when $\mu = 1$. We will see that using the regularization (4.11) for the ultraviolet divergence of the Fredholm determinant in the case $\mu = 1$ introduces some infrared divergences. However, as we will show in detail later, these infrared divergences can be dealt in a similar way as it was done for the two dimensional examples of Ref. [16].

We finally introduce the generalized zeta function defined as

$$Z(s, a) = \sum_{k=0}^{\infty} (a - \lambda_k)^{-s} \quad (4.12a)$$

$$= \frac{1}{\Gamma(s)} \int_0^{\infty} \Theta(t) e^{-at} t^{s-1} dt. \quad (4.12b)$$

The first expression for the generalized zeta function defined as a series is convergent for any s such that $\Re(s) > \mu$ and for any a such that $a \geq \lambda_0$. The second expression (4.12b) where the zeta function is expressed as a Mellin transform of the heat kernel actually allows an analytic continuation of $Z(s, a)$ for $\Re(s) < \mu$ if the heat kernel admits a full asymptotic expansion for $t \rightarrow 0$ of the form (4.2) as explained in Ref. [29]. Note that $Z(s, 0) = Z(s)$, where $Z(s) = \sum_{k=0}^{\infty} (-\lambda_k)^{-s}$ is the zeta function of the sequence $\{\lambda_k\}$. The analytic continuation of the zeta function has the following properties [29] which we will need shortly. $Z(s)$ is meromorphic in the whole complex s plane and has poles at $s = -i_n$ with residue

$$\text{Res } Z(-i_n) = \frac{c_{i_n}}{\Gamma(-i_n)}. \quad (4.13)$$

In particular from Eq. (4.3) we deduce that the first pole is encountered at $s = -i_0 = \mu = d/2$ and has residue $V/[\Gamma(d/2)(4\pi)^{d/2}]$. Notice that this residue is independent of the shape of the manifold: it only depends on its total volume V . Also the negative or zero integers $s = -n$ are regular points of $Z(s)$ and we have [29]

$$Z(-n) = (-1)^n n! c_{-n}. \quad (4.14)$$

The generalized zeta function provides another regularization for the Fredholm determinant of the Laplacian known as the zeta regularization. Indeed differentiating (4.12a) under the sum with respect to the variable s and putting $s = 0$ afterwards (a procedure which is not legal since the expression (4.12a) is convergent only for $\Re(s) > \mu$) formally yields

$$\left. \frac{\partial Z(s, 0)}{\partial s} \right|_{s=0} - \left. \frac{\partial Z(s, a)}{\partial s} \right|_{s=0} = \ln \prod_{k=0}^{\infty} \left(1 - \frac{a}{\lambda_k}\right) \quad (4.15)$$

Strictly speaking this Eq. (4.15) is incorrect and it should be only understood as a formal relation to justify the word “determinant” in the name zeta regularization of the determinant of the Laplacian since the infinite product involved in the r.h.s. is divergent. Notice however the l.h.s. of Eq. (4.15) is well defined once the analytic continuation of $Z(s, a)$ is done with the aid of relation (4.12b).

The zeta regularization of the Laplacian determinant and the Fredholm determinant (4.11) are closely related. In Ref. [29] a general relation between them is found for any sequence of numbers of arbitrary order μ . In our particular case this relation reads

$$\left. \frac{\partial Z(s, 0)}{\partial s} \right|_{s=0} - \left. \frac{\partial Z(s, a)}{\partial s} \right|_{s=0} = \ln \left[\prod_{k=0}^{\infty} \left(1 - \frac{a}{\lambda_k} \right) e^{a/\lambda_k} \right] + a \text{FP}[Z(1)] \quad (4.16)$$

where $\text{FP}[Z(1)]$ denotes the finite part of Z at 1, defined as usual by

$$\text{FP}[Z(s)] = \begin{cases} Z(s) & \text{if } s \text{ is not a pole of } Z \\ \text{FP}[Z(s)] = \lim_{\varepsilon \rightarrow 0} \left[Z(s + \varepsilon) - \frac{\text{Res } Z(s)}{\varepsilon} \right] & \text{if } s \text{ is a pole of } Z \end{cases} \quad (4.17)$$

IV.2 The Connection with the Grand Potential of the Coulomb Systems

As the reader probably noticed, the Fredholm determinant is quite similar to the infinite product that appears in the expression for the grand canonical partition function (2.5) for Coulomb systems in the Debye–Hückel approximation. Our goal in this section is to relate this kind of products with the geometrical information that can be extracted from the asymptotic expansion of the heat kernel.

IV.2.1 The bulk case

First let us mention some points concerning the case of an unconfined system. In this case the eigenvalues $\lambda_n = \lambda_n^0$ and the expression (2.5) for the grand canonical partition function involves precisely the Fredholm determinant (4.11) with $a = \kappa^2$. The exponential terms e^{κ^2/λ_n} that come from the subtraction of the self-energy properly regularize the infinite product $\prod_n [1 - (\kappa^2/\lambda_n)]$. The final result for the grand potential (2.6) and (2.7) is finite and does not depend on any ultraviolet cutoff.

As a side note let us mention that if we were interested in the formulation of Debye–Hückel theory for a system living in four or more dimensions, the expression (2.5) for the bulk grand partition function would not be convergent and it would require the introduction of an ultraviolet cutoff. This is because in dimension $d \geq 4$ the index of the sequence of the Laplacian eigenvalues would be $\mu = d/2 \geq 2$. For this case the correct regularization of the Fredholm determinant would require an additional exponential term as shown in

Eq. (4.10). Physically this means that the bulk properties of a Coulomb system in dimension greater or equal than four, in the Debye–Hückel regime, can only be defined for a system of charged hard spheres or any other charged particles with a short-range potential that cuts the singularity of the Coulomb potential. The inverse of the radius of the particles is the equivalent of the ultraviolet cut-off in our formulation. The bulk thermodynamic properties would depend on the radius of the particles, and diverge if one takes this radius to zero. This can be contrasted with the two- and three-dimensional cases where one can build a Debye–Hückel theory for which the bulk properties have a well defined limit for point-like particles.

As a complement on this remark let us remind the reader that for a three-dimensional system the exact thermodynamic properties, beyond the Debye–Hückel approximation, are not well defined for a system of point-like particles due to the collapse of particles of opposite sign. In two dimensions this collapse problem is less strong: if the thermal energy of the particles is high enough a system of point particles is well defined. On the other hand, the Debye–Hückel approximation is less sensitive to this collapse problem: for two- and three-dimensional systems the bulk properties are well defined for point particles. However as we have seen in the examples, in the three-dimensional case the surface properties are sensitive to the collapse problem and a proper definition of these require the introduction of a short-distance cutoff. For dimensions greater or equal than four the collapse problem appears for the bulk properties even in the Debye–Hückel approximation.

IV.2.2 Zeta regularized grand potential

Now let us consider a confined Coulomb system in the manifold \mathcal{M}_g . Let R be the characteristic size of the manifold. For instance one can define R as $V^{1/d}$ where V is the volume of the manifold. We are interested in the large- R expansion of the grand potential of the system, which can be obtained from Eq. (2.5). In this section we will study an intermediary quantity Ω^* related to the grand potential which we define by

$$\beta\Omega^* = \frac{1}{2} [Z'(0, 0) - Z'(0, \kappa^2)] . \quad (4.18)$$

For obvious reasons (remember Eqs. (4.15) and (2.5)) we will call this quantity the zeta regularized grand potential. The prime in Eq. (4.18) indicates differentiation with respect to the first variable of the zeta function (s).

As we will show below, the large- R expansion of the zeta regularized grand potential is related to the small- t expansion of the heat kernel (4.3). To see this, let us consider a system where all lengths have been rescaled by a factor $1/R$: it is a Coulomb system confined in a manifold of fixed volume equal to 1 but with the same shape as the original system. Let $Z_1(s, a)$ be the generalized zeta function for the spectrum of the Laplace operator for such a manifold and $\Theta_1(t)$ its heat kernel. The subscript 1 refers to a system confined in a volume 1. For

the original system of characteristic size R we will eventually use the subscript R in the spectral functions $Z_R(s, a)$ and $\Theta_R(t)$.

The eigenvalues of the system of size R are the same as those of the system of size 1 multiplied by a factor R^{-2} . Then we have $\Theta_R(t) = \Theta_1(R^{-2}t)$ and $Z_R(s, a) = R^{2s}Z_1(s, aR^2)$. From this we see that an expansion of the heat kernel Θ_R for large- R and fixed argument is the same as an expansion of the heat kernel Θ_1 for small argument.

We have

$$\begin{aligned}\beta\Omega^* &= \frac{1}{2} \left[\frac{\partial}{\partial s} [R^{2s}Z_1(s, 0)]_{s=0} - \frac{\partial}{\partial s} [R^{2s}Z_1(s, \kappa^2 R^2)]_{s=0} \right] \\ &= Z_1(0, 0) \ln R - Z_1(0, \kappa^2 R^2) \ln R - \frac{Z_1'(0, \kappa^2 R^2)}{2} + \frac{Z_1'(0, 0)}{2}\end{aligned}\quad (4.19)$$

where the prime denotes differentiation with respect to the first argument s . The last term is a constant, so we will eventually drop it in the large- R expansion.

From Eq. (4.12b) we can see that a small argument t expansion of the heat kernel $\Theta(t)$ is equivalent to a large argument a expansion of the zeta function $Z(s, a)$. Then using the small argument expansion of the heat kernel (4.2) into Eq. (4.12b) one can obtain in general the large- R expansion [29]

$$Z_1'(0, (\kappa R)^2) \sim \sum_{i_n \notin \mathbb{Z}^- \cup \{0\}} c_{i_n} \Gamma(i_n) (\kappa R)^{-2i_n} - \sum_{m=0}^{[\mu]} c_{-m} \left[\ln(\kappa R)^2 - \sum_{r=1}^m r^{-1} \right] \frac{(-\kappa^2 R^2)^m}{m!}.$$

(4.20)

In this equation the coefficients c_{i_n} are those of the heat kernel expansion (4.2) for a system of size 1 and we use the convention that if m is not any of the exponents i_n of Eq. (4.2) then $c_m = 0$. The first sum runs over all indexes i_n that are not negative or zero integers. Using this equation and [29] $Z_1(0, a) = c_0 - ac_{-1}$ into (4.19) yield the large- R expansion of the zeta regularized grand potential

$$\begin{aligned}\beta\Omega^* &\underset{R \rightarrow \infty}{\sim} -\frac{1}{2} \sum_{i_n \notin \mathbb{Z}^- \cup \{0\}} c_{i_n} \Gamma(i_n) (\kappa R)^{-2i_n} - \kappa^2 R^2 c_{-1} \left[\ln \kappa - \frac{1}{2} \right] \\ &\quad + c_0 \ln(\kappa R) + \frac{1}{2} Z_1'(0, 0)\end{aligned}\quad (4.21)$$

Now we specialize this result for two and three dimensions. In two dimensions from Eq. (4.9) we read $c_{-1} = \tilde{V}/(4\pi)$, $c_{-1/2} = -\tilde{B}/(8\sqrt{\pi})$ and $c_0 = \chi/6$ where $\tilde{V} = V/R^2$ and $\tilde{B} = B/R$ denote the volume (area) and perimeter of the manifold of characteristic size 1. Then we have

$$\beta\Omega_{2D}^* = \frac{\kappa^2 R^2}{4\pi} \left(\frac{1}{2} - \ln \kappa \right) \tilde{V} - \frac{\kappa R}{8} \tilde{B} + \frac{\chi}{6} \ln(\kappa R) + O(1). \quad (4.22)$$

In three dimensions from Eq. (4.3) we have $c_{-3/2} = \tilde{V}/(4\pi)^{3/2}$, $c_{-1} = -\tilde{B}/(16\pi)$ and $c_{-1/2} = (2\tilde{C} + \tilde{D})/[6(4\pi)^{3/2}]$ with \tilde{V} the volume of the system of size 1, \tilde{B} the area of the boundary of system of size 1 and \tilde{C} and \tilde{D}

the curvatura integra and integrated mean curvature for the system of size 1. Replacing this into Eq. (4.21) we have

$$\beta\Omega_{3D}^* = -\frac{\kappa^3 R^3}{12\pi}\tilde{V} + \frac{\kappa^2 R^2}{16\pi}\left[\ln \kappa - \frac{1}{2}\right]\tilde{B} + \frac{\kappa R}{48\pi}(2\tilde{C} + \tilde{D}) + o(R) \quad (4.23)$$

IV.2.3 Connection between the physical grand potential and the zeta regularized grand potential

The excess grand potential Ω^{exc} of the Coulomb system is obtained from Eq (2.5) as

$$\beta\Omega^{\text{exc}} = \frac{1}{2} \ln \left(\prod_m \left(1 - \frac{\kappa^2}{\lambda_m} \right) \prod_n e^{\frac{\kappa^2}{\lambda_n^0}} \right). \quad (4.24)$$

This expression involves a product very similar to the Fredholm determinant (4.11) but it only coincides with it for the bulk case. In general for a confined system they are different. However we can formally make appear the Fredholm determinant F by writing

$$\begin{aligned} \beta\Omega^{\text{exc}} &= \frac{1}{2} \ln \left(\prod_m \left[\left(1 - \frac{\kappa^2}{\lambda_m} \right) e^{\frac{\kappa^2}{\lambda_m}} \right] e^{\sum_n \frac{\kappa^2}{\lambda_n^0} - \sum_m \frac{\kappa^2}{\lambda_m}} \right) \\ &= \frac{1}{2} \ln F(\kappa^2) + \frac{\kappa^2}{2} \left[\sum_m \frac{1}{-\lambda_m} - \sum_n \frac{1}{-\lambda_n^0} \right]. \end{aligned} \quad (4.25)$$

Then we make the connection with the zeta regularized grand potential Ω^* defined in the previous section using Eq. (4.16), so finally

$$\beta\Omega^{\text{exc}} = \beta\Omega^* - \frac{\kappa^2}{2} \text{FP}[Z(1)] + \frac{\kappa^2}{2} \left[\sum_m \frac{1}{-\lambda_m} - \sum_n \frac{1}{-\lambda_n^0} \right]. \quad (4.26)$$

The last two sums are divergent when taken separately. In principle they should be cutoff in a similar way as in the examples. The proper treatment of these sums should be done separately for each dimension $d = 2$ and $d = 3$.

IV.2.4 Two-dimensional case

In two dimensions the divergences of the sums involved in Eq. (4.26) can be dealt in an elegant way by means of the zeta function. The zeta function has a pole at $s = 1$. Remembering Eq. (4.13) and the fact that the residue of the zeta function Z at $s = 1$ for our confined system is equal to the residue of Z^0 at $s = 1$ for an unconfined system we can identify the summations in Eq. (4.26) with

$$\sum_m \frac{1}{-\lambda_m} - \sum_n \frac{1}{-\lambda_n^0} = \lim_{s \rightarrow 1^+} [Z(s) - Z^0(s)] \quad (4.27)$$

Then using the fact that both zeta functions Z and Z^0 have the same residue at $s = 1$ we find that Eq. (4.26) becomes

$$\beta\Omega_{2D}^{\text{exc}} = \beta\Omega_{2D}^* - \frac{\kappa^2}{2} \text{FP}[Z^0(1)]. \quad (4.28)$$

Now the zeta function for an unconfined system reads

$$Z^0(s) = \sum_n \frac{1}{(-\lambda_n^0)^s} = V \int_{\mathbb{R}^2} \frac{d^2\mathbf{k}}{(2\pi)^2} \frac{1}{\mathbf{k}^{2s}} \quad (4.29)$$

However this zeta function cannot be properly defined: if $\Re(s) \leq 1$ the integral is ultraviolet divergent and if $\Re(s) > 1$ it is infrared divergent. Depending on the sign of $\Re(s) - 1$ this zeta function should be regularized with an ultraviolet or infrared cutoff. For our present purposes we need $Z(s)$ defined for $\Re(s) > 1$, then introducing the infrared cutoff $k_{\min} = 2e^{-C}/L$ as in the two dimensional examples of section III and Ref. [16] we have

$$Z^0(s) = \frac{V}{4\pi} \frac{k_{\min}^{2-2s}}{s-1} \quad (4.30)$$

Its finite part at $s = 1$ is

$$\text{FP}[Z^0(1)] = -\frac{V}{2\pi} \ln k_{\min} = -\frac{V}{2\pi} \ln \frac{2e^{-C}}{L}. \quad (4.31)$$

Therefore

$$\beta\Omega_{2D}^{\text{exc}} = \beta\Omega_{2D}^* + \frac{\kappa^2 V}{4\pi} \ln \frac{2e^{-C}}{L}. \quad (4.32)$$

Clearly this extra term only contributes to the bulk grand potential. Finally reporting this into Eq. (4.22) yields the finite-size expansion

$$\beta\Omega_{2D}^{\text{exc}} = \frac{\kappa^2 R^2}{4\pi} \left(\frac{1}{2} - C - \ln \frac{\kappa L}{2} \right) \tilde{V} - \frac{\kappa R}{8} \tilde{B} + \frac{\chi}{6} \ln(\kappa R) + O(1). \quad (4.33)$$

We have obtained the general finite-size expansion of the grand potential for arbitrary confining geometry in two dimensions. We recover from the first term of Eq. (4.33) the bulk grand potential (2.6), from the second term the surface tension already obtained in the examples $\gamma = k_B T \kappa / 8$ and finally the logarithmic finite-size correction $(\chi/6) \ln R$. This constitutes a proof of the existence of this universal finite-size correction for Coulomb systems, in the Debye-Hückel regime, confined in an arbitrary geometry with Dirichlet boundary conditions for the electric potential.

IV.2.5 Three-dimensional case

For a three-dimensional system we must proceed differently to evaluate the sums in Eq. (4.26) as it was done in the two-dimensional case. Here we cannot identify the sums with zeta functions because in three dimensions the definition (4.12a)

of the zeta functions expressed as a sum is only valid for $\Re(s) > 3/2$ and in Eq. (4.26) the sums correspond to $s = 1$. In the two-dimensional case we did not have this problem because the validity of (4.12a) is for $\Re(s) > 1$ and since the residues of both zeta functions are equal we could take the limit $s \rightarrow 1^+$ of the difference of zeta functions and obtain a finite result. Now, in the three-dimensional case, we need the sums for a value $s = 1 < 3/2$ which is far beyond the validity of Eq. (4.12a). Also the corresponding analytic continuations of the zeta functions do not have the same residue at $s = 1$. Indeed the bulk zeta function Z^0 does not have a pole at $s = 1$ in the three-dimensional case but the zeta function Z for the confined system has a pole at $s = 1$ with residue given by Eq. (4.13) which is related to the coefficient c_{-1} corresponding to the surface contribution to the grand potential. This suggests that the difference of the two sums in Eq. (4.26) will not be convergent for the three-dimensional case as it was in the two-dimensional one and it would give a surface contribution to the grand potential.

Let us introduce a truncated version of the zeta function evaluated at $s = 1$,

$$Z_{\text{cut}}(\tilde{\lambda}) = \sum_{|\lambda_k| < \tilde{\lambda}} \frac{1}{-\lambda_k} \quad (4.34)$$

and the corresponding one for the unconfined system

$$Z_{\text{cut}}^0(\tilde{\lambda}) = \sum_{|\lambda_k| < \tilde{\lambda}} \frac{1}{-\lambda_k} = \frac{V}{(2\pi)^3} \int_{|\mathbf{k}|^2 < \tilde{\lambda}} \frac{d^3\mathbf{k}}{\mathbf{k}^2} = \frac{V}{2\pi^2} \tilde{\lambda}^{1/2}. \quad (4.35)$$

Here $\tilde{\lambda} > 0$ is an ultraviolet cutoff for the eigenvalues. The sums in Eq. (4.26) are

$$\sum_m \frac{1}{-\lambda_m} - \sum_n \frac{1}{-\lambda_n^0} = \lim_{\tilde{\lambda} \rightarrow +\infty} \left[Z_{\text{cut}}(\tilde{\lambda}) - Z_{\text{cut}}^0(\tilde{\lambda}) \right]. \quad (4.36)$$

Let us introduce the counting function $\mathcal{N}(\tilde{\lambda})$ which is equal to the number of eigenvalues λ_k which are $|\lambda_k| < \tilde{\lambda}$. The truncated zeta function is related to the counting function by

$$Z_{\text{cut}}(\tilde{\lambda}) = \int_0^{\tilde{\lambda}} \frac{\mathcal{N}'(\lambda)}{\lambda} d\lambda \quad (4.37)$$

with $\mathcal{N}'(\lambda)$ the derivative (in the sense of the distributions) of $\mathcal{N}(\lambda)$. On the other hand the derivative of the counting function and the heat kernel are related by a Laplace transform

$$\Theta(t) = \int_0^\infty e^{-t\lambda} \mathcal{N}'(\lambda) d\lambda \quad (4.38)$$

Then, from the asymptotic expansion of the heat kernel (4.2) for $t \rightarrow 0$, we can obtain the first terms of the asymptotic expansion of $\mathcal{N}'(\tilde{\lambda})$ for $\tilde{\lambda} \rightarrow +\infty$

$$\mathcal{N}'(\tilde{\lambda}) \underset{\tilde{\lambda} \rightarrow \infty}{\sim} \frac{c_{-3/2}}{\Gamma(3/2)} \tilde{\lambda}^{1/2} + c_{-1} + o(1) = \frac{V}{(2\pi)^2} \tilde{\lambda}^{1/2} - \frac{B}{16\pi} + o(1) \quad (4.39)$$

Reporting this into Eq. (4.37) we find the asymptotic behavior of the truncated zeta function for $\tilde{\lambda} \rightarrow \infty$

$$Z_{\text{cut}}(\tilde{\lambda}) = \frac{V}{2\pi^2} \tilde{\lambda}^{1/2} - \frac{B}{16\pi} \ln \tilde{\lambda} + O(1) \quad (4.40)$$

Then we have

$$Z_{\text{cut}}(\tilde{\lambda}) - Z_{\text{cut}}^0(\tilde{\lambda}) = -\frac{B}{16\pi} \ln \tilde{\lambda} + O(1) = -\frac{B}{8\pi} \ln K_{\text{max}} + O(1) \quad (4.41)$$

where we introduced $K_{\text{max}} = \tilde{\lambda}^{1/2}$ to make the connection with the examples of section III. We see that the divergences are not completely canceled now as opposed to the two-dimensional case. There remains an ultraviolet divergence which contributes to the surface tension (proportional to B the area of the boundary of the manifold). This is the same kind of divergence that we have found in the three-dimensional examples in section III and it is due to the strong attraction of the particles to their images as explained earlier.

Finally collecting the results from Eqs. (4.23), (4.26), and (4.41) the finite-size expansion of the grand potential reads

$$\beta\Omega_{3D}^{\text{exc}} = -\frac{\kappa^3 R^3}{12\pi} \tilde{V} + \frac{\kappa^2 R^2}{16\pi} \left[\ln \frac{\kappa}{K_{\text{max}}} + O((K_{\text{max}})^0) \right] \tilde{B} + \frac{\kappa R}{48\pi} (2\tilde{C} + \tilde{D}) + o(R). \quad (4.42)$$

From this very general calculation we recover the bulk grand potential (2.7), the surface tension $\gamma = k_B T (\kappa^2/16\pi) \ln[\kappa/K_{\text{max}}] + O(1)$ which is ultraviolet divergent. Also we find the perimeter correction to the grand potential (the term proportional to R) which depends on the curvatura integra C and the integrated mean curvature D .

In the example of section III of the three-dimensional Coulomb system confined in a ball we have found a perimeter correction to $\beta\Omega$ equal to $\kappa R/3$. For a ball of radius one in the flat space \mathbb{R}^3 the curvatura integra is $\tilde{C} = 0$ and the mean curvature computed from Eq. (4.8) is $\tilde{J} = 4$ and the integrated mean curvature is $\tilde{D} = 16\pi$. Then the correction predicted by Eq. (4.42), $\kappa R(2\tilde{C} + \tilde{D})/(48\pi) = \kappa R/3$, is in agreement with the explicit result found in the example. For the other example of the Coulomb system confined in the thick spherical shell, the agreement of our general result (4.42) with the explicit calculation of section III is also straightforward.

IV.3 System Confined in a Square Domain

The above analysis is valid for a confining manifold with smooth boundary. However it can easily be generalized for a manifold with a boundary with corners. As an illustration let us consider the case of a two-dimensional Coulomb system confined in a square domain of side R and subjected to Dirichlet boundary conditions for the electric potential.

Conformal field theory predicts that in the case of a two-dimensional critical system confined in a geometry with corners in the boundary, it appears

a contribution to the free energy (times the inverse temperature) equal to $[\theta/(24\pi)](1 - (\pi/\theta)^2) \ln R$ for each corner with interior angle θ [7]. In the case of a square $\theta = \pi/2$ and the contribution per corner equals $\frac{\pi/2}{24\pi}(1 - (2\pi/\pi)^2) \ln R = -(1/16) \ln R$. Then the total contribution of the four corners is $-(1/4) \ln R$. If the similarity of conducting Coulomb systems with critical systems holds then we should expect a finite-size correction to the grand potential times β equal to $(1/4) \ln R$ for Coulomb systems.

The eigenvalues for this case can be found easily by separation of variables expressing the Laplace operator in rectangular coordinates and solving the eigenvalue equation. The spectrum for a system in a square of side equal to 1 is given by $\lambda_{n,l} = -\pi^2 (n^2 + l^2)$, $n = 1, 2, \dots$ and $l = 1, 2, \dots$. The heat kernel is

$$\Theta_1(t) = \sum_{k=0}^{\infty} e^{t\lambda_k} = \left(\sum_{n=1}^{\infty} e^{-\pi^2 n^2 t} \right)^2 \quad (4.43)$$

which can be expressed in terms of the Jacobi theta function

$$\vartheta_3(u|\tau) = \sum_{n=-\infty}^{+\infty} e^{i\pi\tau n^2} e^{2\pi n u i} \quad (4.44)$$

as

$$\Theta_1(t) = \frac{1}{4} [\vartheta_3(0|i\pi t) - 1]^2 \quad (4.45)$$

The heat kernel expansion for $t \rightarrow 0$ can be found using Jacobi imaginary transformation [31]

$$\vartheta_3(u|\tau) = (-i\tau)^{-1/2} e^{u^2/(i\pi\tau)} \vartheta_3\left(\frac{u}{\tau} \middle| -\frac{1}{\tau}\right). \quad (4.46)$$

This gives

$$\Theta_1(t) = \frac{1}{4} \left[-1 + (\pi t)^{-1/2} \left(1 + 2 \sum_{n=1}^{\infty} e^{-n^2/t} \right) \right]^2 \quad (4.47)$$

The asymptotic expansion for $t \rightarrow 0$ is

$$\Theta_1(t) = \frac{1}{4\pi t} - \frac{1}{2\sqrt{\pi t}} + \frac{1}{4} + O\left(\frac{e^{-1/t}}{t}\right) \quad (4.48)$$

Comparing with expression (4.9) for a smooth boundary we recognize the first two terms: the volume (area) ($\tilde{V} = 1$) and the surface (perimeter) ($\tilde{B} = 4$) terms which are the same. The constant term on the other hand is now equal to $1/4$. Applying the same argument developed above for the general case to this heat kernel we see that this constant term is the one that gives the coefficient of the logarithmic finite-size correction for the grand potential. Then the finite-size expansion for this geometry reads

$$\beta\Omega = \beta\Omega_b - \frac{\kappa B}{8} + \frac{1}{4} \ln(\kappa R) + o(\ln R) \quad (4.49)$$

with Ω_b given by Eq. (2.6) with $V = R^2$ and the perimeter of the square $B = 4R$ with R the length of a side. The logarithmic finite-size correction is in agreement with the one predicted by conformal field theory with the appropriate change of sign.

V Summary and Perspectives

We have illustrated with several examples how to apply the method of Ref. [16] to find the grand potential of a Coulomb system in the low coupling regime and confined by ideal conductor boundaries. We considered several examples: in two dimensions the slab and in three dimensions the slab, the ball and a thick spherical shell. The method can easily be adapted to other geometries. In all the examples we also computed the finite-size expansion of the grand potential. For the slab geometries, in three and two dimensions, we recover a universal algebraic finite-size correction predicted in Ref. [1]. For two-dimensional fully confined systems the finite-size expansion exhibits a universal logarithmic term similar to the one predicted for critical systems by conformal field theory [16].

We have also extended the method to confined systems of arbitrary shape with a smooth boundary. For this general case we showed how the heat kernel expansion for small argument for the considered geometry is related to the large-size expansion of the grand potential of the Coulomb system. From this, we recovered the expressions for the bulk grand potential and the surface tension which agree with those found in the specific examples. Regarding the finite-size corrections, in the case of two dimensions we proved the existence of a universal logarithmic finite-size correction for the grand potential times β equal to $(\chi/6) \ln R$ with χ the Euler characteristic of the confining manifold. For three dimensional systems we also found a general prediction for the perimeter correction to the grand potential but it is not universal (it depends on the Debye length).

The general treatment for arbitrary confining geometry exposed here is done for Dirichlet boundary conditions but can also be adapted for other kind of boundary conditions. For example for ideal dielectric boundary conditions, i.e. Neumann boundary conditions for the electric potential, the heat kernel expansion is very similar to Eq. (4.3) except that the surface term changes of sign [18]. As a consequence the surface tension of a Coulomb system confined by ideal dielectric boundaries would be minus the surface tension of a Coulomb system confined by ideal conductor boundaries in the low coupling regime. For a confining geometry with smooth boundary the finite-size expansion will read as in Eqs. (4.33) and (4.42) for two and three dimensions respectively except for a change of sign in the surface tension term.

The method exposed in Ref. [16] and used here can be extended to compute the density profiles and correlation functions. An example of such application for the case of a slab geometry in three dimensions can be found in Ref. [19].

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